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Non-additivity in the solvation enthalpies of substituted phenols and estimation of their enthalpies of vaporization/sublimation at 298.15 K

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ABSTRACT

In this work we have developed an additivity scheme for the solvation enthalpy calculation of systems with solute–solvent hydrogen bond interactions. A simple additivity scheme was modified with the contribution of hydrogen bonding on the values of solvation enthalpy. This contribution was calculated using the Iogansen equation which connected the enthalpy of hydrogen bonds with the frequency shifts of O—H stretching vibrations. The efficiency of the scheme for calculating the enthalpies of solvation was tested on the substituted phenols and 1-naphthol in three solvents (acetonitrile, tetrahydrofurane and 1.4-dioxane). We have determined the vaporization/sublimation enthalpies of the substituted phenols and 1-naphthol directly at 298.15 K using experimentally measured solution enthalpies and estimated values of solvation enthalpies. Obtained values of vaporization/sublimation enthalpies are in good agreement with available literature data.

1. Introduction

Sublimation enthalpy is an important parameter of a pure substance. Traditional methods for the determination of this parameter are based on the investigation of the process of phase transition from standard state to gas. In this way problems arise, well documented elsewhere [1,2]. In the series of our previous papers [3–8] we have shown that sublimation/vaporization enthalpies can be determined using the solution calorimetry method. This approach is based on the calculation of the solvation enthalpy of solute A_i in solvent S and the measurement of the enthalpy of solution at 298.15 K. The enthalpy of solvation can be calculated using linear dependences between molar refraction and enthalpy solvation in various solvents [3,4,6–8]. In the works [3,4] we have determined enthalpies of vaporization/sublimation of aromatic hydrocarbons and their halogen-derivatives. The modified equation for the calculation of the solvation enthalpy of branched-chain alkyl aromatic and aliphatic compounds in cyclohexane was proposed in [6–8].

A simpler method for the estimation of the enthalpy of solvation of aromatic hydrocarbons and their derivatives was offered in [5,9]. It is based on the group contributions into the solvation enthalpy of the fragments of a molecule. This method of calculation is in good agreement with experimental enthalpies of the solvation of aromatic compounds.

However, in some cases the solvation enthalpy cannot be calculated using the group contribution method, for example in the case of solute–solvent hydrogen bonding. H-bonding enthalpy is included into the solvation enthalpy of solute A_i in solvent S. The values of contribution depend on the electronic and steric effects of the substituents [10]. Because of this the solvation enthalpy of proton donor solute A_i in a proton acceptor solvent S is not an additive function of group contributions. In the present paper we show, how non-additivity contribution, into the solvation enthalpy of substituted phenols in acetonitrile, tetrahydrofuran and 1.4-dioxane, can be estimated using IR spectroscopy.

2. Experimental part

2.1. Materials

All samples were of commercial origin with the mass fraction purities better than 0.97. 4-Nitrophenol and 1.4-dihydroxybenzene were purified by recrystallization from ethanol. 1.3-Dihydroxybenzene was recrystallized from benzene. 3-Chlorophenol was distillated under reduced pressure. Other samples for solution calorimetry were used without purification (see Table S1)

All solvents were purified before use according to [11]. The purity of samples was analyzed using an Agilent 7890 B gas chromatograph (GC)

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